Available online at www.sciencedirect.com

ScienceDirect

Procedia Chemistry 1 (2009) 1584–1589

Procedia Chemistry

www.elsevier.com/locate/procedia

INTERACTION BETWEEN C_{60} FULLERENE AND ALKALI METALS DEMONSTRATING SUPERCONDUCTIVITY

Timur S. Jakubov* and David E. Mainwaring

School of Applied Sciences, Royal Melbourne Institute of Technology
124 La Trobe Street, Melbourne 3001, Australia

Abstract

A discret summation method [1] has been used to calculate the van der Waals dispersion interactions between an alkali metal atom and individual C_{60} fullerene molecules, as well as between an intercalated alkali metal atom and the face-centred-cubic lattice of solid fullerite. It is known [2, 3] that the conductivities observed in the doped C_{60} films vary considerably for different alkali atoms. Our interest was to investigate any correlation between these conductivities and the long range potential field behaviour. In the present study, we have obtained interaction potential curves of the C_{60} fullerene molecule including within its cage, as well the potential field topography within the overall C_{60} fullerite solid unit cell. We have found that for all intercalated alkali metals, except Cs, there are voids within the unit-cell of fullerite where the dopant experiences attractive interactions. Whereas on the other hand, inside the fullerene cage only Li and Na experience attractive forces. Importantly, it has been shown that the localization of the crystallographic sites [4] of doped alkali metals in fullerite coincide with the potential energy minima of long range van der Waals forces.

Keywords: Fullerene; Fullerite; Alkali metal; Dispersion interaction; Superconductivity

* Corresponding author. Tel.: +(613) 9925 2125; fax: +(613) 9925 3747.
E-mail address: timur.jakubov@rmit.edu.au

1876-6196/09
doi:10.1016/j.proche.2009.11.007

1. Introduction

There are extensive studies that show that alkali metal-doped C_{60} fullerenes provide electrical conductivities at room temperature comparable to n-type polymers [2] as well as superconducting materials with transition temperatures that range up to 33K [5]. Superconductivity in alkali doped C_{60} is a consequence of a high density of states at the Fermi surface [6]. Charge transfer and electron-phonon interactions have been shown by Chen et al. [5] to be responsible for superconductivity in force-field studies that replace electrons by 2,3, and 4-body potentials plus long range van der Waals interactions. The most important feature of the solid fullerite pure C_{60} lattice is that of a molecular insulator, whereas the doped compound demonstrates metalic conductivity [4]. It was initially suggested [2] and more recently experimentally confirmed [4] that the doped atoms are locked into a two fixed position; the (0.25, 0.25, 0.25) tetrahedral site and the (0, 0, 0.5) octahedral site. The stoichiometry of A_3C_{60} compound indicates that alkali atoms occupy both such sites. Our investigation below, is focussed on calculations of the dispersion field distribution within the C_{60} fullerite cell, for which the interaction potentials between the C_{60} fullerene molecule and alkali metals atom was calculated initially.

2. Results and discussion

2.1 Direct calculation of the C_{60} fullerene – alkali metal interaction potential

The interaction potential between C_{60} fullerene molecules and alkali metal atoms are calculated by a direct summation method. The potential was considered as the sum of the interactions between all carbon atoms of the C_{60} fullerene molecule with the alkali metal atom as discribed by the Lennard-Jones (6-12) expression:

$$U(z_k) = 4e\left[\left(\frac{s}{R_i}\right)^{12} - \left(\frac{s}{R_i}\right)^{6}\right] \qquad (1)$$

where z_k is the current distance between centres of fullerene molecule and alkali metal atom and R_i is the current distance between centres of metal atom and i-th carbon atom of the fullerene molecule. The interaction potential was found by calculation of the following sum, which was performed for k varying from 0 to 2000

$$\mathrm{Sum}(U(k,i),\ i = 1...60) \qquad (2)$$

where, for each k, calculations were carried out for each fixed distance $z_k = z_0 + 0.01k$.

The pair-wise atom-atom potential was considered to be additive. The Lennard-Jones 12 – 6 potential parameters for corresponding atoms adopted in our calculations were taken from following sources: C – C [7], the binding energy of Li – Li, Na – Na, K – K, Rb – Rb [8] and Cs – Cs [9]; the equilibrium distances were calculated from corresponding values of the lattice parameters at 5 K [10, 11,12].For the C_{60} – C_{60} interaction we employed the results of our previous calculations [1]. The interaction parameters between dissimilar atoms have been derived from the Lorentz-Berthelot mixing rules [13,14].

Generally interaction potentials depend on the mutual orientation of the approaching fullerene molecule and an alkali atom. Here calculations were performed for the case when the alkali atom approaches the fullerene molecule along the axis passing through the centre of fullerene and centre of a hexagonal face. The calculated interaction potentials for lithium, sodium, potassium, rubidium, and caesium as function of this distance, including within the fullerene cage, are given in Fig. 1(a) and Fig. 1(b).

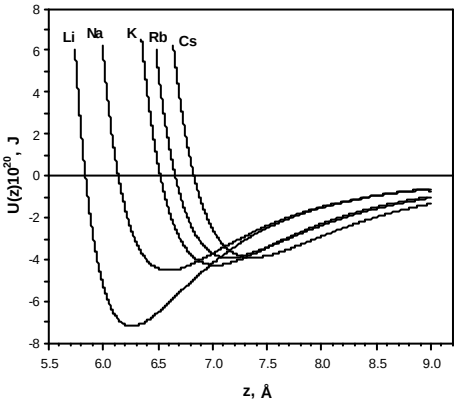

Figure 1(a). Interaction potentials between alkali atoms and C_{60} fullerene molecule outside the C_{60}.

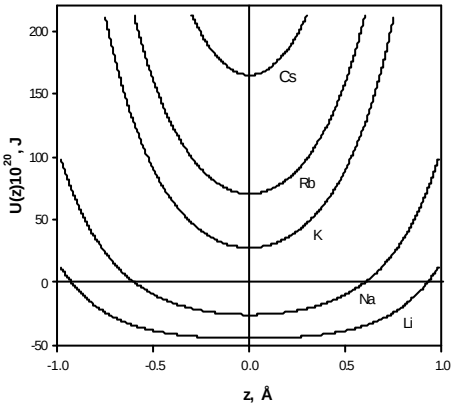

Figure 1(b). Interaction potentials between alkali atoms and C_{60} fullerene molecule inside the C_{60} cage.

The interaction parameters between fullerene and all alkali metals deduced from our calculations are shown in Table 1. As can be seen in Fig. 1(b) and Table 1 only lithium and sodium inside the fullerene cage exist in an area where attractive forces dominate while all alkali metals at the C_{60} surface boundary exist in areas with very high potential barriers (i.e. 5 – 6 orders of magnitude greater than the depth of the potential well)

Table 1
Parameters of the dispersion interaction between C_{60} fullerene molecule and alkali metals

	Li	Na	K	Rb	Cs
$U(0)\cdot 10^{20}$, J	– 44.3099	– 25.5646	27.5097	70.3005	164.675
σ_{in} , Å	0.923994	0.597947			
z_{max}, Å	3.2648	3.2648	3.2648	3.2647	3.2647
$U(z_{max})\cdot 10^{20}$, J	146320	258319	824461	1145370	1866787
σ_{out} , Å	5.83487	6.13673	6.52171	6.65767	6.82952
z_{min} , Å	6.25985	6.5934	7.0216	7.1734	7.3656
$U(z_{min})\cdot 10^{20}$, J	– 7.17564	– 4.51611	– 4.25566	– 3.93482	– 3.89748

preventing penetration of alkali metal atoms into the C_{60} fillerene cage.

2.2 Interaction between an intercalated alkali metal and lattice of solid fullerite

Solid C_{60} (fullerite) is molecular crystal formed by a relatively small van der Waals cohesive energy. For temperatures above a structural phase transition at 249 K, the C_{60} molecules are arranged in a face centred cubic (FCC) crystal with lattice parameter a_0 = 14.17 ± 0.01 Å [15]. From the calculation we derive a value of a_0 = 14.1825 Å. Schematically the FCC unit-cell of the fullerite lattice is presented in Fig. 2, where the locations of doped alkali atoms also are shown.

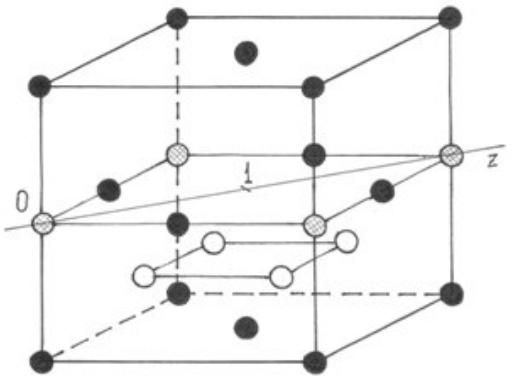

Figure 2. Schematic representation of the FCC unit-cell of the fullerite lattice. Black circles indicate the position of C_{60} molecules; hatched and open circles represent the intercalated potassium atoms at octahedral and tetrahedral sites respectively.

Of particular interest is the determination of the topography of the dispersion force field within the fullerite unit-cell and its correlation between the locations of intercalated alkali atoms as well as the magnitude of the dispersion interaction energy. The interaction potential curves calculated between alkali atoms and

fullerite in central area of the unit-cell are shown in Fig. 3. Because C_{60} molecules freely are rotating in the fullerite crystal, we have employed values of the $C_{60} - C_{60}$ interaction parameters averaged for all C_{60} orientations. As may be seen, all atoms except ceasium experience attractive forces in fullerite lattice. Figure 4 demonstrates interaction potential behaviour between the potassium atom and the whole fullerite lattice, as the potassium atom moves from octohedral sites (hatched circles in Fig. 2) to the centre of unit-cell where two relatively deep minima can be seen. A minimun potential energy is also observed at the eight tetrahedral sites with co-ordinates ¼, ¼, ¼ illustrated in Fig. 2 (open circles).

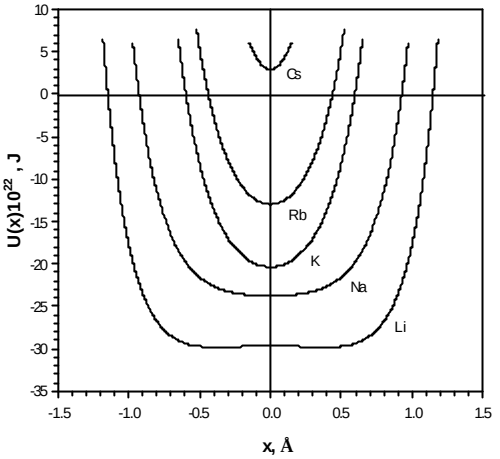

Figure 3. Interaction potentials between alkali atoms and fullerite in the central area of the cell.

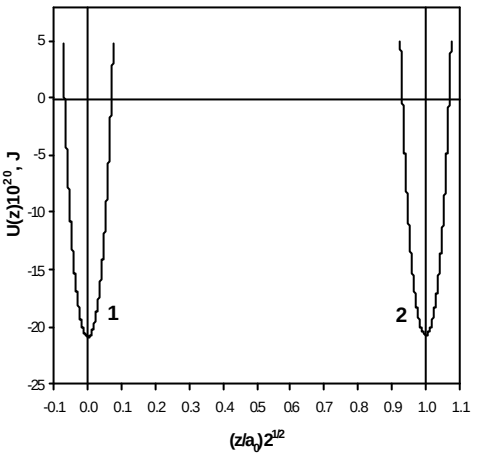

Figure 4. Interaction potentials between potassium atom and whole fullerite lattice atthe octahedral sites (1) and at the centre of the cell (2).

Thus the minima of dispersion potential energy in the voids of the fullerite lattice coincide withthe sites of crystallographic localization of the doped alkali atoms. The topographic relationships occur for cations of these metals when the outer electrons of the doped metal atom form a nearly free electron gas within the fullerite lattice.

3. Conclusions

Summarizing, the results of our direct calculations of the dispersion energy interaction between alkali metals and the C_{60} fullerene molecule as well as the fullerite lattice indicate that the weak van der Waals interactions play an integral part in the structural arrangement of alkali doped compounds of the form A_3C_{60}

that demonstrate superconductivity at reduced temperatures.

References

[1] T.S. Jakubov, D.E. Mainwaring, Adsorption, 14, (2008) 727.

[2] R.C. Haddon, A.F. Hebard, M.J. Rosseinsky, D.W. Murphy, S.J. Duclos, K.B. Lyons, B. Müller, J.M. Rosamilia, R.M. Fleming, A.R. Kortan, S.H. Glarum, A.V. Makhija, A.J. Muller, R.H. Eick, S.M. Zahurak, R. Tycko, G. Dabbagh, F.A. Thiel, Nature, 350 (1991) 320.

[3] A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, D.W. Murphy, S.H. Glarum, T.T.M. Palstra, A.P. Ramirez, A.R. Kortan, Nature, 350 (1991) 600.

[4] P.W. Stephens, L. Mihaly, P.L. Lee, R.L. Whetten, S.-M. Huang, R. Kaner, F. Deiderich, K. Holczer, Nature, 351 (1991) 632.

[5] G. Chen, Y. Guo, N. Karasawa, W.A. Goddard III, Phys. Rev. B, 48 (1993) 13959.

[6] T.T.M. Palstra, O. Zhou, Y. Iwasa, P.E. Suewski, R.M. Fleming, B.R. Zegarski, Solid State Commun., 93 (1995) 327.

[7] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids, Vol. 1. Fundamentals,* Clarendon Press, Oxford, 1984.

[8] J. Mitroy, M.W.J. Bromley, Phys. Rev. A, 68 (2003) 052714.

[9] M. Marinescu, H.R. Sadeghpour, A. Dalgarno, Phys. Rev.A, 49 (1994) 982.

[10] C.S. Barrett; Acta Cryst., 9 (1956) 671.

[11] Ch. Kittel, Introduction to solid state physics, 8-th ed., Hoboken, N.J., John Wiley, 2005.

[12] S. Zhen, G.J. Davies, Phys. Stat. Sol., 78 (1983) 595

[13] H. A . Lorentz, *Ann. Phys. Chem.*, 12, (1881) 127

[14] D. Berthelot, *Comp. Rend. Acad. Sci. Paris*, 126 (1889) 1703.

[15] O. Zhou, J.E. Fischer, N. Coustel, S. Kycia, Q. Zhu, A.R. McGhie, W.J. Romanow, J.P. McCauley Jr, A.B. Smith III, D.E. Cox, 351 (1991) 462.